

PCT
 WELTORGANISATION FÜR GEISTIGES EIGENTUM
 Internationales Büro
 INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
 INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)



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<p>(21) Internationales Aktenzeichen: PCT/EP98/07690</p> <p>(22) Internationales Anmeldedatum: 28. November 1998 (28.11.98)</p> <p>(30) Prioritätsdaten: 197 54 418.5 9. Dezember 1997 (09.12.97) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten außer US): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): VOIGT, Michael [DE/DE]; Düsseldorf Strasse 8, D-47239 Duisburg (DE). JBSCHKE, Kurt [DE/DE]; Ansbacher Strasse 24, D-40597 Düsseldorf (DE). ECKERT, Armin [DE/DE]; Heinrich-von-Kleist-Strasse 13, D-68766 Hockenheim (DE). MÜLLER, Volker [DE/DE]; Schützenweg 7, D-76661 Philippsburg (DE).</p> <p>(74) Gemeinsamer Vertreter: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).</p>	<p>(81) Bestimmungsstaaten: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO Patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Veröffentlicht Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</p>	
<p>(54) Title: STABILIZED MOLDING COMPOUNDS COMPRISED OF BIOLOGICALLY DEGRADABLE MATERIALS</p> <p>(54) Bezeichnung: STABILISIERTE FORMMASSEN BIOLOGISCH ABBAUBARER MATERIALIEN</p> <p>(57) Abstract</p> <p>The invention relates to stabilized thermoplastic molding compounds comprised of biologically degradable polymers which are stabilized against hydrolytic and microbial degradation and a method for producing concentrates based on thermoplastic biologically degradable polymers. The invention also relates to a method for producing hydrolysis stabilized and antimicrobial or microbistatic acting thermoplastic biologically degradable molding compounds as well as to the utilization of the inventive stabilized molding compounds as biologically degradable materials for the production of semi-finished goods, films, injection molded parts, monofilaments, multifilaments, fibers, non-wovens and wovens. In addition, the invention relates to the molded bodies produced from the molded compounds such as semi-finished goods, films, injection molded parts, monofilaments, multifilaments, fibers, non-wovens and wovens.</p> <p>(57) Zusammenfassung</p> <p>Gegenstand der vorliegenden Erfindung sind gegen hydrolytischen und mikrobiellen Abbau stabilisierte thermoplastische Formmassen aus biologisch abbaubaren Polymeren, ein Verfahren zur Herstellung von Konzentraten auf Basis thermoplastischer biologisch abbaubarer Polymere, ein Verfahren zur Herstellung hydrolysestabilisierter und antimikrobiell oder mikrobistatisch wirkender thermoplastischer, biologisch abbaubarer Formmassen sowie die Verwendung der erfindungsgemäß stabilisierten Formmassen als biologisch abbaubare Werkstoffe für die Herstellung von Halbzeugen, Folien, Spritzgußformteilen, Mono- und Multifilamenten, Fasern, Vliesen und Geweben sowie die daraus hergestellten Formkörper bzw. Halbzeuge, Folien, Spritzgußformteile, Mono- und Multifilamente, Fasern, Vliese und Gewebe selbst.</p>		

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Stabilized moulding compositions of biologically degradable materials

5 The present invention relates to thermoplastic moulding compositions, which are stabilized against hydrolytic and microbial degradation, of biologically degradable polymers, a process for the preparation of concentrates based on thermoplastic biologically degradable polymers, a process for the preparation of thermoplastic biologically degradable moulding compositions which are stabilized against hydrolysis and have an antimicrobial or microbistatic action, and the use of the moulding compositions stabilized according to the invention as biologically degradable materials
10 for the production of semi-finished products, films, injection mouldings, mono- and multifilaments, fibres, nonwovens and woven fabrics, and the shaped articles or semi-finished products, films, injection mouldings, mono- and multifilaments, fibres, nonwovens and woven fabrics themselves produced therefrom.

15 Biologically degradable plastics are known (see, for example, EP-A 561 224, EP-A 641 817). Hydrolysis stabilizers and microbicides and microbistatic active compounds are likewise known (see, for example, 9th corrected and improved edition of Römpf Chemie Lexikon on CD-ROM, version 1.0, Thieme Verlag, key words "Stabilisatoren", "Mikrobizid", "Preventol", "Carbodiimid").

20 Many biologically degradable materials are generally accessible to a hydrolytic degradation mechanism which proceeds not only in the presence of microorganisms living in the soil, water and compost, but also at a slow to moderate rate in the presence of moisture already during storage of the granules and during use of the
25 products produced therefrom.

The object of the present invention is to control and in particular to slow down this premature degradation and loss of properties of the materials, without thereby impairing the desired biological degradation of the finished components after use to a
30 noticeable extent.

An object is furthermore to increase the storage stability and prolong the usable life, in particular under damp climate conditions, of the semi-finished products and finished components produced from the moulding compositions according to the invention. It
35 has now been found that, by addition of additives and stabilizers to biologically degradable polymers, the start of the biological and hydrolytic degradation is delayed

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such that long-term applications, e.g. in the building sector or in landscaping, are possible with these materials.

5 The invention provides thermoplastic biologically degradable moulding compositions comprising biologically degradable polymers and at least one stabilizer chosen from group A1) and A2)

10 A1) 0 to 50 wt.%, preferably 0.001 to 30 wt.%, and particularly preferably 0.05 to 5 wt.%, based on the total mixture, of stabilizers chosen from at least one of the group consisting of hydrolysis stabilizers, such as e.g. aliphatic or aromatic monomeric, oligomeric or polymeric carbodiimides, such as, for example, urethanized carbodiimides, N,N'-dicyclohexylcarbodiimide, N-glycidylphthalimide, 1,3-bis(1-methyl-1-isocyanato-ethyl)benzene with terminal isocyanate-, urea- and/or urethane groups, bis(trimethylsilyl)-carbodiimide, 15 polyfunctional oxazolines, polyfunctional epoxides and polyfunctional isocyanates, preferably chosen from the group consisting of polymeric or polymer-bonded carbodiimides, which are obtainable, for example, from the polymerization, which takes place by conventional catalysts with splitting off of carbon dioxide, of aromatic or aliphatic isocyanates, such as, for example, 20 2,6-diisopropylphenyl isocyanate, 1,3,5-trisopropyl-2,4-diisocyanatobenzene, naphthalene 1,5-diisocyanate, 2,4-diisocyanato-3,5-diethyltoluene, 4,4'-methylene-bis(2,6-diethylphenyl isocyanate), 4,4'-methylene-bis(2-ethyl-6-methylphenyl isocyanate), 4,4'-methylene-bis(2-isopropyl-6-methylphenyl isocyanate), 4,4'-methylene-bis(2,6-diisopropylphenyl isocyanate) and 4,4'-methylene-bis(2-ethyl-6-methylcyclohexyl isocyanate) and 25

30 A2) 0 to 50 wt.%, preferably 0.001 to 30 wt.%, and particularly preferably 0.01 to 5 wt.%, based on the total mixture, of a stabilizer chosen from at least one of the group consisting of antimicrobial agents, for example thiurams, thiophthalimides, sulfamides, urea derivatives, triazole derivatives, triazoline derivatives, benzimidazole derivatives, benzimidazolylcarbamic acid derivatives, aryl sulfones, sulfonylsulfamides, phenols and phenolates, thiobenzothiazole derivatives, amino alcohols, isothiazolinones, benzothiazoles and pyrethroids and 35

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- B) 0 to 85 wt.%, based on the total mixture, of fillers and reinforcing substances, preferably naturally occurring mineral, synthetic inorganic or naturally occurring organic substances based on renewable raw materials or synthetic organic and metallic substances or a mixture of several of these constituents.

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Carbodiimides which are approved for contact with foodstuffs or a mixture thereof are particularly preferred.

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The invention also provides additive concentrates based on the biologically degradable polymers themselves. Concentrates to date, which are based, for example, on polyethylene or polyesters, do not meet the requirement of complete biological degradation. Moreover, the melting ranges of conventional concentrates, for example based on aromatic polyesters, and the biologically degradable, usually aliphatic or only partly aromatic, plastics differ widely, so that a homogeneous incorporation of the conventional known concentrates into biologically degradable polymers is made difficult. The concentrates based on biologically degradable plastics have the advantage of good compatibility of the materials and the associated homogeneous distribution of the additives in the particular matrix. The concentrates in general comprise up to 40 wt.%, preferably 1 to 30 wt.%, in particular 5 to 20 wt.% stabilizer, based on the total mixture.

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Suitable biologically degradable polymers are, for example, aliphatic polyesters or copolyesters, aromatic polyesters or copolyesters, aromatic-aliphatic copolyesters, polycarbonates, polyester-carbonates, aliphatic or partly aromatic polyester-urethanes, polyester-amides, polyether-amides, polyether-ester-amides, cellulose ethers, cellulose ether-esters, thermoplastic starch, starch derivatives or copolymers or a mixture of these components.

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The following polymers are preferably suitable:

Aliphatic or partly aromatic polyesters from

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- A) aliphatic bifunctional alcohols, preferably linear C_2 to C_{10} -dialcohols, such as, for example, ethanediol, butanediol or hexanediol, particularly preferably butanediol, and/or optionally cycloaliphatic bifunctional alcohols, preferably having 5 or 6 C atoms in the cycloaliphatic ring, such as, for example,

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- 5 cyclohexanedimethanol, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 8,000, preferably up to 4,000, and/or optionally small amounts of branched bifunctional alcohols, preferably C₃-C₁₂-alkyldiols, such as, for example, neopentylglycol, and additionally optionally small amounts of alcohols of higher functionality, such as, for example, 1,2,3-propanetriol or trimethylolpropane, and from aliphatic bifunctional acids, preferably C₂-C₁₂-alkyldicarboxylic acids, such as, for example and preferably, succinic acid or adipic acid, and/or optionally aromatic bifunctional acids, such as, for example, terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and additionally optionally small amounts of acids of higher functionality, such as, for example, trimellitic acid, or
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- 15 B) building blocks with acid and alcohol functional groups, preferably having 2 to 12 C atoms in the alkyl chain, for example hydroxybutyric acid, hydroxyvaleric acid or lactic acid, or derivatives thereof, for example ε-caprolactone or dilactide, or a mixture and/or a copolymer of A and B, the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;
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Aliphatic or partly aromatic polyester-urethanes from

- 25 C) aliphatic bifunctional alcohols, preferably linear C₂ to C₁₀-dialcohols, such as, for example, ethanediol, butanediol or hexanediol, particularly preferably butanediol, and/or optionally cycloaliphatic bifunctional alcohols, preferably with a C₅- or C₆-cycloaliphatic ring, such as, for example, cyclohexanedimethanol, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 4,000, preferably up to 1,000, and/or optionally small amounts of branched bifunctional alcohols, preferably C₃-C₁₂-alkyldiols, such as, for example, neopentylglycol, and additionally optionally small amounts of alcohols of higher functionality, preferably C₃-C₁₂-alkylpolyols, such as, for example, 1,2,3-propanetriol or trimethylolpropane, and from aliphatic bifunctional acids, preferably C₂-C₁₂-alkyldicarboxylic acids, such as, for example and preferably,
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succinic acid or adipic acid, and/or optionally aromatic bifunctional acids, such as, for example, terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and additionally optionally small amounts of acids of higher functionality, such as, for example, trimellitic acid, or

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- D) building blocks with acid and alcohol functional groups, preferably having 2 to 12 C atoms, for example hydroxybutyric acid, hydroxyvaleric acid or lactic acid, or derivatives thereof, for example ϵ -caprolactone or dilactide, or a mixture and/or a copolymer of C and D,

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the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;

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- E) the reaction product of C and/or D with aliphatic and/or cycloaliphatic bifunctional isocyanates and additionally optionally isocyanates of higher functionality, having preferably 1 to 12 C atoms, or 5 to 8 C atoms in the case of cycloaliphatic isocyanates, e.g. tetramethylene diisocyanate, hexamethylene diisocyanate or isophorone diisocyanate, optionally additionally with linear and/or branched and/or cycloaliphatic bifunctional alcohols and/or alcohols of higher functionality, preferably C_2 - C_{12} -alkyldi- or -polyols, or 5 to 8 C atoms in the case of cycloaliphatic alcohols, e.g. ethanediol, hexanediol, butanediol or cyclohexanedimethanol, and/or optionally additionally with linear and/or branched and/or cycloaliphatic bifunctional amines and/or amino alcohols and/or amines and/or amino alcohols of higher functionality, having preferably 2 to 12 C atoms in the alkyl chain, e.g. ethylenediamine or aminoethanol, and/or optionally further modified amines or alcohols, such as, for example, ethylenediaminoethane-sulfonic acid, as the free acid or as a salt,

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the ester content C) and/or D) being at least 75 wt.%, based on the sum of C), D) and E).

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Aliphatic or aliphatic-aromatic polyester-carbonates from

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- F) aliphatic bifunctional alcohols, preferably linear C_2 to C_{10} -dialcohols, such as, for example, ethanediol, butanediol or hexanediol, particularly preferably butanediol, and/or optionally cycloaliphatic bifunctional alcohols, preferably

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5 having 5 to 8 C atoms in the cycloaliphatic ring, such as, for example, cyclohexanedimethanol, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 4,000, preferably up to 1,000, and/or optionally small amounts of branched bifunctional alcohols, preferably with C_2 - C_{12} -alkyldicarboxylic acids, such as, for example, neopentylglycol, and additionally optionally small amounts of alcohols of higher functionality, such as, for example, 1,2,3-propanetriol or trimethylolpropane, and from aliphatic bifunctional acids, such as, for example and preferably, succinic acid or adipic acid, and/or optionally aromatic bifunctional acids, such as, for example, terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and additionally optionally small amounts of acids of higher functionality, such as, for example, trimellitic acid, or

15 G) building blocks with acid and alcohol functional groups, preferably having 2 to 12 C atoms in the alkyl chain, for example hydroxybutyric acid, hydroxyvaleric acid or lactic acid, or derivatives thereof, for example ϵ -caprolactone or dilactide, or a mixture and/or a copolymer of F) and G),

20 the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;

25 H) a carbonate content which is prepared from aromatic bifunctional phenols, preferably bisphenol A, and carbonate donors, for example phosgene, or a carbonate content which is prepared from aliphatic carbonic acid esters or derivatives thereof, such as, for example, chlorocarbonic acid esters, or aliphatic carboxylic acids or derivatives thereof, such as, for example, salts and carbonate donors, for example phosgene,

30 the ester content F) and/or G) being at least 70 wt.%, based on the sum of F), G) and H);

Aliphatic or partly aromatic polyester-amides or polyetherester-amides from

35 I) aliphatic bifunctional alcohols, preferably linear C_2 - to C_{10} -dialcohols, such as, for example, ethanediol, butanediol or hexanediol, particularly preferably

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- 5 butanediol, and/or optionally cycloaliphatic bifunctional alcohols, preferably having 5 to 8 C atoms, such as, for example, cyclohexanedimethanol, and/ or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 10,000, preferably up to 8,000, particularly preferably up to 5,000, and/or optionally small amounts of branched bifunctional alcohols, preferably C₃-C₁₂-alkyldiols, such as, for example, neopentylglycol, and additionally optionally small amounts of alcohols of higher functionality, preferably C₃-C₁₂-alkylpolyols, such as, for example, 10 1,2,3-propanetriol or trimethylolpropane, and from aliphatic bifunctional acids, preferably having 2 to 12 C atoms in the alkyl chain, such as, for example and preferably, succinic acid or adipic acid, and/or optionally aromatic bifunctional acids, such as, for example, terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and additionally optionally small amounts of 15 acids of higher functionality, such as, for example, trimellitic acid, or
- 20 K) building blocks with acid and alcohol functional groups, preferably having 2 to 12 C atoms in the carbon chain, for example hydroxybutyric acid, hydroxyvaleric acid or lactic acid, or derivatives thereof, for example ε-caprolactone or dilactide,
- or a mixture and/or a copolymer of I) and K), the aromatic acids making up a content of not more than 50 wt.%, based on all the acids,
- 25 L) an amide content from aliphatic and/or cycloaliphatic bifunctional and/or optionally small amounts of branched bifunctional amines, preferred compounds being linear aliphatic C₇- to C₁₀-diamines, and additionally optionally small amounts of amines of higher functionality, and among the amines preferably hexamethylenediamine or isophoronediamine, and particularly preferably hexamethylenediamine, and from linear and/or 30 cycloaliphatic bifunctional acids, preferably having 2 to 12 C atoms in the alkyl chain, or C₅ or C₆-ring in the case of cycloaliphatic acids, preferably adipic acid, and/or optionally small amounts of branched bifunctional and/or optionally aromatic bifunctional acids, such as, for example, terephthalic acid, 35 isophthalic acid or naphthalenedicarboxylic acid, and additionally optionally

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small amounts of acids of higher functionality, preferably having 2 to 10 C atoms, or

- 5 M) an amide content of building blocks with acid and amine functional groups, preferably having 4 to 20 C atoms in the cycloaliphatic chain, preferably ω -lauryllactam or ϵ -caprolactam, particularly preferably ϵ -caprolactam,

- 10 or a mixture of L) and M) as the amide content, the ester content I) and/or K) being at least 30 wt.%, based on the sum of I), K), L) and M), and preferably the weight content of the ester structures is 30 to 70 wt.% and the content of the amide structures is 70 to 30 wt.%.

The polyether-ester-amides are built up, in particular, from the following monomers:

- 15 oligomeric polyols comprising polyethylene glycols, polypropylene glycols, polyglycols, built up randomly or in block form, from mixtures of ethylene oxide or propylene oxide, or polytetrahydrofurans having molecular weights (weight-average) of between 100 and 10,000 and

- 20 monomeric diols, preferably C_2 - C_{12} -alkyl-diols, in particular C_2 - C_6 -alkyldiols, for example ethylene glycol, 1,4-butanediol, 1,3-propanediol or 1,6-hexanediol, and at least one monomer chosen from the group consisting of

- 25 dicarboxylic acids, preferably C_2 - C_{12} -, particularly preferably C_2 - C_6 -alkyl-dicarboxylic acids, for example oxalic acid, succinic acid or adipic acid, also in the form of their particular ethers (methyl, ethyl etc.)

C_2 - C_{12} -alkylhydroxycarboxylic acids and lactones, such as caprolactone, inter alia,

- 30 amino alcohols having 2 to 12 carbon atoms in the alkyl chain, for example ethanolamine or propanolamine

cyclic lactams having 5 to 12, preferably 6 to 11 C atoms, such as ϵ -caprolactam or lauryllactam etc.

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ω -aminocarboxylic acids having 6 to 12 C atoms in the alkyl chain, such as aminocaproic acid etc.

5 mixtures (1:1 salts) of C_7 - C_{12} -alkyldicarboxylic acids, for example adipic acid or succinic acid, and C_7 - C_{12} -alkyldiamines, for example hexamethylenediamine or diaminobutane.

10 Polyesters having either hydroxyl or acid end groups and molecular weights of between 300 and 10,000 can also be employed as the ester-forming component.

The proportion of the ether and ester contents in the polymer is in general 5 to 85 wt.%, based on the total polymer.

15 The polyether-ester-amides according to the invention in general have an average molecular weight (Mw determined by gel chromatography in cresol against polystyrene standard) of 10,000 to 300,000, preferably 15,000 to 150,000, in particular 15,000 to 100,000.

20 All the acids can also be employed in the form of derivatives, such as, for example, acid chlorides or esters, both as monomeric and as oligomeric esters.

25 The synthesis of the biologically degradable polyester-amides according to the invention can be carried out both by the "polyamide method" by stoichiometric mixing of the starting components, if appropriate with the addition of water, and subsequent removal of water from the reaction mixture, and by the "polyester method" by stoichiometric mixing of the starting components and addition of an excess of diol, with esterification of the acid groups and subsequent transesterification or transamidation of these esters. In this second case, in addition to water, the excess diol is also distilled off again. The synthesis by the "polyester method" described is preferred.

30 The polycondensation can furthermore be accelerated by using known catalysts. Both the known phosphorus compounds which accelerate polyamide synthesis and acid or organometallic catalysts for esterification and also combinations of the two are possible for acceleration of the polycondensation.

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It should be ensured that the catalysts adversely influence neither the biological degradability or compostability nor the quality of the resulting compost. The polycondensation to give polyester-amides can furthermore be influenced by using lysine, lysine derivatives or other products which branch by amide formation, such as, for example, aminoethylaminoethanol, which both accelerate the condensation and lead to branched products (see, for example, DE-A 38 31 709).

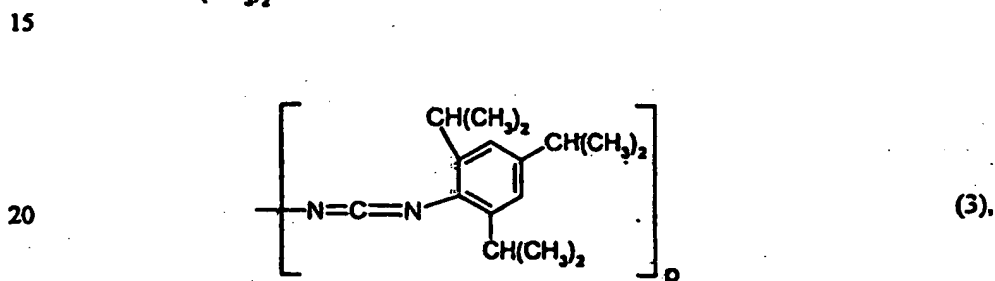
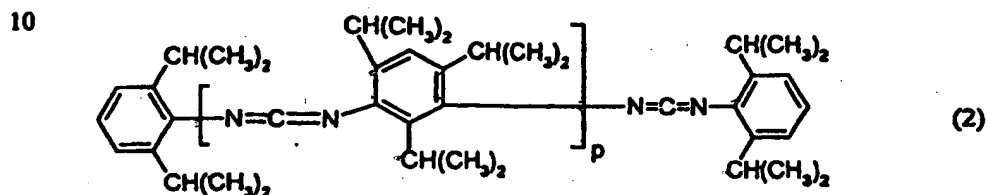
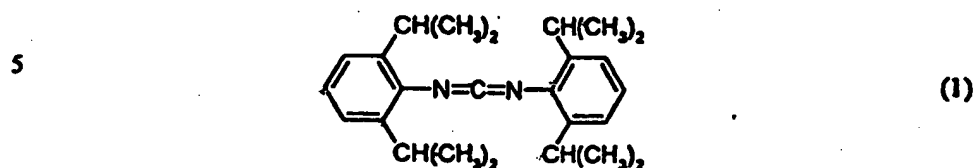
The preparation of polyesters, polyester-carbonates and polyester-urethanes is generally known or is carried out analogously to known processes (cf. e.g. EP-A 304 787, WO 95/12629, WO 93/13154, EP-A 682 054 and EP-A 593 975).

The polyesters, polyester-urethanes, polyester-carbonates or polyester-amides according to the invention can furthermore comprise 0.1 to 5 wt.%, preferably 0.1 to 1 wt.%, of branching agents (cf. also the description of the polymers). These branching agents can be e.g. trifunctional alcohols, such as trimethylolpropane or glycerol, tetrafunctional alcohols, such as pentaerythritol, or trifunctional carboxylic acids, such as citric acid. The branching agents increase the melt viscosity of the polyester-amides according to the invention to the extent that extrusion blow moulding with these polymers becomes possible. The biological degradation of these materials is not impeded as a result.

The biologically degradable/compostable polyester-urethanes, polyesters, polyester-carbonates and polyester-amides as a rule have a molecular weight of at least 10,000 g/mole, and in general have a random distribution of the starting substances in the polymer. In the polyurethane-typical polymer build-up optionally of C) and D) and of E), a completely random distribution of the monomer building blocks is not always to be expected.

A particularly preferred polycarbodiimide is the aromatic polycarbodiimide which is substituted with isopropyl groups in the o-position relative to the carbodiimide groups, i.e. in the 2,6- or 2,4,6-position on the benzene nucleus. The polycarbodiimides present preferably have an average molecular weight of 1,500 to 15,000, but in particular 9,000 to 12,000. In particular, by addition of small amounts of aromatic and/or aliphatic (poly)carbodiimides, it is possible to increase the thermooxidative stability such that the end group contents of the biologically degradable plastics are reduced and a hydrolytic stability of the biologically degradable plastics is achieved.

The following carbodiimides may be mentioned as examples:



wherein

25 p is determined by the molecular weight.

The carbodiimides can be prepared by processes known per se (e.g. DE-AS 25 37 685, DE-AS 11 56 401, DE-AS 24 19 968 and FR 1 180 307).

30 Fillers and reinforcing substances which are suitable according to the invention can be minerals, such as, for example, kaolin, chalk, gypsum, mica, lime or talc, or naturally occurring substances, such as, for example, starch or modified starch, cellulose or cellulose derivatives or cellulose products, wood flour or natural fibres, such as, for example, hemp, flax, sisal, rape or ramie. Metallic fillers which can furthermore be
35 employed are iron powder, iron oxides, iron alloys (e.g. ferrotitanium,

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ferromolybdenum, ferromanganese), tungsten, tungsten carbide, ferrotungsten, molybdenum, manganese, cobalt, copper, zinc, tin or bismuth or combinations thereof.

5 The biologically degradable/completely compostable polyester-urethanes, polyesters, polyester-carbonates and polyester-amides according to the invention can be equipped with conventional additives. It is thus possible to use modifying agents and/or processing auxiliaries, such as, for example, nucleating agents, plasticizers, mould release auxiliaries, flameproofing agents, impact modifiers, stabilizers, for example for stability to heat, stability to oxidation and stability to UV and light, colour-imparting agents (e.g. pigments) or other additives which are usual in the thermoplastics field, but it should be ensured that complete compostability is not impaired or that the substances which remain, for example mineral auxiliaries, are harmless in the compost. The additives are in general added in an amount of up to 15 wt.%, based on the total mixture.

15 The moulding compositions according to the invention are biologically degradable, preferably completely degradable. Those moulding compositions which can be classified as completely degradable in accordance with DIN 54 900 are particularly preferred.

20 The biologically degradable/completely compostable polyester-urethanes, polyesters, polyester-carbonates and polyester-amides according to the invention can also be mixed with further blend partners, e.g. thermoplastic starch, but it should be ensured that complete compostability is not impaired or that the substances which remain, for example mineral auxiliaries, are harmless in the compost.

25 Further blend partners which can be employed for further fields of use in which biological degradability is not necessary are:

30 polyethylene, modified polyethylenes, such as, for example, an LDPE modified with maleic anhydride, a fluorine thermoplastic, such as, for example, polytetrafluoroethylene, tetrafluoroethylene/hexafluoropropylene copolymer, tetrafluoroethylene/perfluoroalkoxyvinyl ether copolymer, ethylene/tetrafluoroethylene copolymer, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, 35 polyvinylidene fluoride, polyvinyl fluoride, polyfluoroalkoxyalkane, tetrafluoroethylene/hexafluoropropylene/vinylidene fluoride copolymer, amorphous

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perfluorinated polymers, polyvinyl chloride, polyvinylidene chloride, a polypropylene, a polyvinyl alcohol, a polyvinyl acetate, a partly hydrolysed polyvinyl acetate, a polyvinyl ether, a polyether, a polyacrylate, an aliphatic polyester or copolyester, an aromatic polyester or copolyester, an aromatic-aliphatic copolyester, a polycarbonate, a polyester-carbonate, a partly aromatic polyurethane, an aliphatic polyurethane, a polyester-urethane, a polyamide, a polyester-amide, a polyether-amide, a polyether-ester-amide, a cellulose ether, a cellulose ether-ester, a starch derivative or a copolymer or a mixture of several of those mentioned.

10 The blend partners can be employed up to a content of 99 wt.%, preferably up to 70 wt.%, based on the total amount of the moulding composition.

15 The invention also provides a process for the preparation of the moulding compositions according to the invention, characterized in that the individual components and optionally further additives (conventional additives) are mixed in a known manner and the mixture is subjected to melt compounding and melt extrusion at elevated temperatures, preferably of 150 to 300°C, in conventional units, such as internal kneaders, extruders and twin-screw extruders.

20 The invention also provides a process for the preparation of the moulding compositions according to claims 1 to 15, wherein the biologically degradable polymer is mixed with a concentrate of biologically degradable polymer and at least one stabilizer A1) or A2) and optionally component B) and additives, and the mixture is subjected to melt compounding and melt extrusion at elevated temperature.

25 Extruders which can be employed are, for example:
a densely combing twin-screw extruder with screws which interlock completely, a single-screw extruder for high-performance extrusion which operates by the stator-rotor principle (e.g. Staromix® from Reifenhäuser), a triple-screw extruder, a continuously/discontinuously operating CO kneader and a continuous dispersion kneader with a slow-running rotor-stator combination (e.g. KEX, Drais, Mannheim).

35 The invention also provides the use of the moulding compositions according to the invention for the production of semi-finished products, films, in particular hygiene films, rubbish bags, roof underlining webs and films as a constituent of clothing, injection mouldings, in particular plant pots, plant clamps and plant binders,

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multifilaments, monofilaments, fibres, in particular cut fibres and fibres for coating heat-sealable filter papers, nonwovens and woven fabrics, in particular geotextiles, protective works clothing and automobile interior lining, and the articles themselves.

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Examples**Example 1**

- 5 A polyester-amide (e.g. BAK® 1095 from Bayer AG) was melted with an aromatic polycarbodiimide (e.g. Stabaxol® P100 from Rhein Chemie Rheinau GmbH) at 170°C to 190°C on a twin-screw extruder of the type ZSK from Werner & Pfleiderer, Stuttgart, with an L/D ratio of >35 and special kneading elements, with at least the first cooled intake zone. The strands extruded in this way were cooled in a water bath, granulated and dried.

BAK®1095 is a polyester-amide of adipic acid, butanediol and caprolactam having an ester/amide weight ratio of 70/30, randomly copolycondensed with a relative solution viscosity of 2.78, measured on a 1 wt.% solution in meta-cresol at 20°C.

BAK®2195 is a polyester-amide of 32.3 wt.% adipic acid, 11.7 wt.% 1,4-butanediol, 15.0 wt.% diethylene glycol, 41 wt.% AH salt, randomly copoly-condensed with a relative solution viscosity of 2.8, measured on a 1 wt.% solution in m-cresol at 20°C.

Table 1

Concentrates with hydrolysis stabilizer (the numerical data of the composition designate wt.%)

Concentrate	A	B	C	D	E
BAK® 1095	90		90		
BAK® 2195		90		90	90
Stabaxol® P	10	10			
Stabaxol® P100			10	10	
Stabaxol® P200					10
Rel. solution viscosity	2.78	2.72	3.91	3.27	2.66

Example 2

BAK®2195 is injection moulded to test bars (80*10*4 mm) as a mixture with a concentrate prepared according to example 1. The bars are stored at 60°C in water, to which 0.02 wt.% sodium azide is added as a biocide to maintain sterility. The results are shown in table 2.

Table 2: Results of the storage in water at 60°C

Storage time/d	BAK 2195 unstabilized	BAK 2195 + 10% concentrate B from example 1 (corresponds to 1% Stabaxol P)	BAK 2195 + 10% concentrate D from example 1 (corresponds to 1% Stabaxol P100)	BAK 2195 + 10% concentrate from example 1 (corresponds to 1% Stabaxol P200)
0	2.66	2.67	2.75	2.76
24	2.76	2.54	2.66	2.82
48	2.33	2.47	2.49	2.85
70		2.42	2.48	
72				2.71
144	2.15			
168	2.15	2.32	2.40	2.47
336		2.06	2.08	2.13
504	1.71			1.80
648	1.59			
672				1.63
816		1.59	1.61	
840				1.47

Patent claims

1. Thermoplastic moulding compositions comprising biologically degradable polymers and at least one stabilizer chosen from group A1) and A2):
- 5
- A1) 0 to 50 wt.%, based on the total mixture, of stabilizers chosen from at least one of the group consisting of hydrolysis stabilizers,
- and/or
- 10
- A2) 0 to 50 wt.%, based on the total mixture, of a stabilizer chosen from at least one of the group consisting of antimicrobial agents, and
- B) 0 to 85 wt.%, based on the total mixture, of fillers and reinforcing substances.
- 15
2. Moulding compositions according to claim 1, comprising biologically degradable polymers chosen from at least one of the group consisting of aliphatic (co)polyesters, aromatic-aliphatic (co)polyesters, polycarbonates, polyester-carbonates, aliphatic or partly aromatic polyester-urethanes, polyester-amides, polyether-amides, polyether-ester-amides, cellulose ethers, cellulose ether-esters, thermoplastic starch and starch derivatives or copolymers and/or mixtures thereof.
- 20
3. Moulding compositions according to claim 1 and 2, wherein the polymers are chosen from a polymer of the group consisting of:
- 25
- aliphatic or partly aromatic polyesters from
- 30
- A) aliphatic bifunctional alcohols, and/or optionally cycloaliphatic bifunctional alcohols, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 8,000, and/or optionally small amounts of branched bifunctional alcohols, and additionally optionally small amounts of alcohols of higher functionality, and from aliphatic bifunctional acids,
- 35

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and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality or

- 5 B) building blocks with acid and alcohol functional groups or derivatives thereof, or a mixture and/or a copolymer of A and B, the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;

10 aliphatic or partly aromatic polyester-urethanes from

- 15 C) aliphatic bifunctional alcohols, and/or optionally cycloaliphatic bifunctional alcohols, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 4,000, and/or optionally small amounts of branched bifunctional alcohols, and additionally optionally small amounts of alcohols of higher functionality, and from aliphatic bifunctional acids, and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality, or

- 20 D) building blocks with acid and alcohol functional groups, or derivatives thereof, or a mixture and/or a copolymer of C and D,

25 the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;

the reaction product of C and/or D and

- 30 E) aliphatic and/or cycloaliphatic bifunctional isocyanates and additionally optionally isocyanates of higher functionality, optionally additionally with linear and/or branched and/or cycloaliphatic bifunctional alcohols and/or alcohols of higher functionality, and/or optionally additionally with linear and/or branched and/or cyclo-aliphatic bifunctional amines and/or amino alcohols and/or amines and/or amino alcohols of higher functionality and/or optionally further modified amines or alcohols,
- 35

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the ester content C) and/or D) being at least 75 wt.%, based on the sum of C), D) and E);

aliphatic or aliphatic-aromatic polyester-carbonates from

5

F) aliphatic bifunctional alcohols, and/or optionally cycloaliphatic bifunctional alcohols, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 4,000, and/or optionally small amounts of branched bifunctional alcohols, and additionally optionally small amounts of alcohols of higher functionality, and from aliphatic bifunctional acids, and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality or

10

15

G) building blocks with acid and alcohol functional groups or derivatives thereof, or a mixture and/or a copolymer of F) and G),

20

the aromatic acids making up a content of not more than 50 wt.%, based on all the acids;

with

25

H) a carbonate content which is prepared from aromatic bifunctional phenols and carbonate donors, or a carbonate content which is prepared from aliphatic carbonic acid esters or derivatives thereof and carbonate donors

30

the ester content F) and/or G) being at least 70 wt.%, based on the sum of F), G) and H);

aliphatic or partly aromatic polyester-amides or polyether-ester-amides from

35

I) aliphatic bifunctional alcohols, and/or optionally cycloaliphatic bifunctional alcohols, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene

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glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 10,000, and/or optionally small amounts of branched bifunctional alcohols, and additionally optionally small amounts of alcohols of higher functionality, and from aliphatic bifunctional acids, and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality or

K) building blocks with acid and alcohol functional groups or derivatives thereof,

or a mixture and/or a copolymer of I) and K), the aromatic acids making up a content of not more than 50 wt.%, based on all the acids,

and

L) an amide content from aliphatic and/or cycloaliphatic bifunctional and/or optionally small amounts of branched bifunctional amines, and additionally optionally small amounts of amines of higher functionality, and from linear and/or cycloaliphatic bifunctional acids, and/or optionally small amounts of branched bifunctional and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality, or

M) an amide content of building blocks with acid and amine functional groups,

or a mixture of L) and M) as the amide content, the ester content I) and/or K) being at least 30 wt.%, based on the sum of I), K), L) and M).

4. Moulding compositions according to claim 3, comprising polyether-ester-amides built up from the following monomers:

oligomeric polyols comprising polyethylene glycols, polypropylene glycols, polyglycols, built up randomly or in block form, from mixtures of ethylene oxide or propylene oxide, or polytetrahydrofurans having molecular weights (weight-average) of between 100 and 10,000 and

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monomeric diols,

and at least one monomer chosen from the group consisting of

C₂-C₁₂-alkyl-dicarboxylic acids, also in the form of their particular esters,

bifunctional acids and additionally optionally small amount of acids of higher functionality, or

an amide content of building blocks with acid and amide functional groups, having 4 to 20 C atoms in the cycloaliphatic chain,

or a mixture of L) and M) as the amide content, the ester content I) and/or K) being at least 30 wt.%, based on the sum of I), K), L) and M).

5. Moulding compositions according to claims 1 to 3, wherein the polyester-amides are built up from

I) aliphatic bifunctional alcohols, and/or optionally cycloaliphatic bifunctional alcohols, and/or, instead of some or all of the diols, monomeric or oligomeric polyols based on ethylene glycol, propylene glycol or tetrahydrofuran or copolymers thereof having molecular weights of up to 10,000, and/or optionally small amounts of branched bifunctional alcohols, and additionally optionally small amounts of alcohols of higher functionality, and from aliphatic bifunctional acids, and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality or

K) building blocks with acid and alcohol functional groups or derivatives thereof,

or a mixture and/or a copolymer of I) and K), the aromatic acids making up a content of not more than 50 wt.%, based on all the acids,

and

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- 5 L) an amide content from aliphatic and/or cycloaliphatic bifunctional and/or optionally small amounts of branched bifunctional amines, and additionally optionally small amounts of amines of higher functionality, and from linear and/or cycloaliphatic bifunctional acids, and/or optionally small amounts of branched bifunctional and/or optionally aromatic bifunctional acids and additionally optionally small amounts of acids of higher functionality, or
- 10 M) an amide content of building blocks with acid and amine functional groups,
- 15 or a mixture of L) and M) as the amide content, the ester content I) and/or K) being at least 30 wt.%, based on the sum of I), K), L) and M).
6. Moulding compositions according to one of the preceding claims, comprising 0.001 to 30 wt.%, based on the total mixture, of stabilizers according to A1).
- 20 7. Moulding compositions according to one of the preceding claims, comprising 0.005 to 5 wt.% A1).
8. Moulding compositions according to one of the preceding claims, comprising 0.001 to 30 wt.% A2).
- 25 9. Moulding compositions according to one of the preceding claims, comprising 0.01 to 5 wt.% A2).
- 30 10. Moulding compositions according to one of the preceding claims, wherein component A1) is chosen from one or more stabilizers chosen from the group consisting of monomeric, oligomeric or polymeric carbodiimides, polyfunctional oxazolines, polyfunctional epoxides and polyfunctional isocyanates.
- 35 11. Moulding composition according to claim 10, wherein the carbodiimides are chosen from urethanized carbodiimides, N,N'-dicyclohexylcarbodiimide, N-

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glycidylphthalimide, 1,3-bis(1-methyl-1-isocyanato-ethyl)benzene with terminal isocyanate-, urea- and/or urethane groups, bis(trimethylsilyl)-carbodiimide, polymeric and/or polymer-bonded carbodiimides, which are obtainable from the polymerization, which takes place with splitting off of carbon dioxide, of aromatic or aliphatic isocyanates.

12. Moulding composition according to claim 11, wherein the isocyanates are chosen from the group consisting of 2,6-diisopropylphenyl isocyanate, 1,3,5-triisopropyl-2,4-diisocyanatobenzene, naphthalene 1,5-diisocyanate, 2,4-diisocyanato-3,5-diethyltoluene, 4,4'-methylene-bis(2,6-diethylphenyl isocyanate), 4,4'-methylene-bis(2-ethyl-6-methylphenyl isocyanate), 4,4'-methylene-bis(2-isopropyl-6-methylphenyl isocyanate), 4,4'-methylene-bis(2,6-diisopropylphenyl isocyanate) and 4,4'-methylene-bis(2-ethyl-6-methylcyclohexyl isocyanate).
13. Moulding composition according to one of the preceding claims, comprising one or a mixture of antimicrobial agents, chosen from the group consisting of the structural class of thiurams, thiophthalimides, sulfamides, urea derivatives, triazole derivatives, triazoline derivatives, benzimidazole derivatives, benzimidazolylcarbamic acid derivatives, aryl sulfones, sulfenylsulfamides, phenols and phenolates, thiobenzothiazole derivatives, aminoalcohols, isothiazolinones, benzothiazoles and pyrethroids.
14. Moulding compositions according to one of the preceding claims, wherein component B) is chosen from the group consisting of naturally occurring, mineral, synthetic inorganic or naturally occurring organic and metallic fillers and reinforcing substances or mixtures thereof.
15. Moulding compositions according to one of the preceding claims, comprising additives chosen from at least one of the group consisting of modifying agents, processing auxiliaries, plasticizers, mould release auxiliaries, flameproofing agents, impact modifiers, stabilizers and colour-imparting agents.
16. Process for the preparation of the moulding compositions according to claim 1 to 15, wherein the individual components and optionally further additives are

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mixed and the mixture is subjected to melt compounding and melt extrusion at elevated temperature.

- 5 17. Process for the preparation of the moulding compositions according to claim 1 to 15, wherein the biologically degradable polymers are mixed with a concentrate of biologically degradable polymer and at least one stabilizer A1) or A2) and optionally component B) and additives, and the mixture is subjected to melt compounding and melt extrusion at elevated temperature.
- 10 18. Use of the moulding compositions according to claim 1 to 15 for the production of semi-finished products, films, roof underlining webs, films as a constituent of clothing, injection mouldings, multifilaments, monofilaments, fibres, woven fabrics and automobile interior lining.
- 15 19. Semi-finished products, films, roof underlining webs, films as a constituent of clothing, injection mouldings, multifilaments, monofilaments, fibres, woven fabrics and automobile interior lining obtainable from moulding compositions according to claims 1 to 15.

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PUB-NO: JP410306215A

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TITLE: MATERIAL FOR PREVENTING ADHESION OF ORGANISM

PUBN-DATE: November 17, 1998

INVENTOR-INFORMATION:

NAME

COUNTRY

NUMATA, MASAFUMI

SUZUKI, TARO

INT-CL (IPC): [C08 L 101/00](#); [B05 D 5/08](#); [C08 K 3/36](#); [C09 D 5/16](#)

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a material for preventing adhesion of organisms having a specific contact angle against water, excellent in soil preventing effect for a long time in water, safe to human body and not polluting the environment by blending a hydrophobic material with a biodegradable resin.

SOLUTION: This material for preventing adhesion of organisms showing 80-180° contact angle of surface thereof against water, is obtained by blending (A) a biodegradable resin e.g. an aliphatic polyester such as a polycaprolactone and a polyamide such a polyglutamic acid with (B) a hydrophobic material (especially preferable, an amorphous silica surface-treated to have hydrophobicity) obtained by coating the surfaces of inorganic particles such as a silica, an alumina, a magnesia or a fluorine-based compound with a silicone, a silane and a paraffin or processing with a suitable treating material, to give a hydrophobic property to the material itself, by 1-90 pts.wt. component (B), preferably 20-60 pts.wt. based on 100 pts.wt. component (A).

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